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(54) **Polyolefins.**

(57) Olefins are polymerized with use of a catalyst composed of a specified catalyst component and a specified modified organoaluminum compound. The catalyst component is derived from mutual contact of an inorganic porous oxide, an aluminum-based of $Al(OR')_nX_{3-n}$ and a transition metal compound of R'_nMX_r . The organoaluminum compound has Al-O-Al bonds in the molecule. Bulk density and particle shape qualities are greatly improved among important physical properties.

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This invention relates to olefinic homopolymers or copolymers having unique physical characteristics. More particularly, the invention relates to a process for the production of such polyolefins using a selected mode of polymerization and a specified catalyst therefor.

A certain catalyst has recently been reputed as particularly suitable for use in homopolymerizing ethylene and also in copolymerizing ethylene with other different α -olefins. It is made up of a metallocene-based component and a methylalumoxane compound as disclosed for instance in Japanese Patent Laid-Open Publication No. 58-19309. The catalyst of this character is rather high in activity per transition metal and capable of producing ethylene homopolymers of narrower molecular weight distributions and ethylene- α -olefin copolymers of narrower composition distributions and lesser stickinesses on the surfaces of the ultimate moldings.

The foregoing catalyst, however, has a drawback in that in gas phase polymerization it will in most cases form objectionable polymer blocks as deposits on the wall or stirrer in a reactor. This literally poses an obstacle to continuous polymerization. In Japanese Patent Laid-Open Publication Nos. 61-296008 and 61-108610 it has been proposed, in an effort to solve the above problem, to support the catalyst component on an inorganic oxide carrier but with insufficient catalytic activity. Japanese Patent Laid-Open Publication Nos. 63-51407 and 1-101315 each teach the use of an activating compound as a cocatalyst so as to improve catalytic activity.

Though acceptably high in activity in terms of transition metals, the above catalysts of the prior art are not wholly satisfactory as the resulting polymer is susceptible to small bulk density and inadequate particle shape. Both great bulk density and good particle shape are important determinants of possible continuous runs of polymerization particularly under solvent-free, gas-phase conditions. There is a strong demand for production methods of polyolefins of the above desired qualities.

The present invention seeks to provide a new process for producing polyolefins in the presence of a specific catalyst which enables polymerization reaction in continuous fashion and with high catalytic activity even in gas phase polymerization.

Olefin homopolymers according to the invention are great in bulk density and optimum in particle shape. Ethylene- α -olefin copolymers in particular have, in addition to the aforesaid physical properties, narrowed molecular weight distribution, increased die swell ratio and reduced surface stickiness. Also noticeably, similar copolymers are available with superior heat resistance and heat sealability qualities in the case of use of titanium as a catalyst component metal. The last-mentioned copolymers have a bimodal peak of melting points at high and low temperature sides as determined by differential scanning calorimetry.

Many other objects and advantages of the invention will become apparent from the following description.

More specifically, the invention provides a process for producing polyolefins which comprises homopolymerizing an olefin or copolymerizing two or more different olefins in the presence of a catalyst comprising a solid catalyst component and a modified organoaluminum compound, the solid catalyst component derived by mutually contacting (a) an inorganic porous oxide, (b) a compound of the formula $Al(OR^1)_nX_{3-n}$ where R^1 is a hydrocarbon group of 1 to 24 carbon atoms, X is a halogen atom, and n is $0 < n \leq 3$, and (c) a compound of the formula $R^2_pMX_r$, where M is a Group IVa metal, R^2 is a cyclopentadienyl, substituted cyclopentadienyl, indenyl or substituted indenyl group or an aralkyl group of 7 to 24 carbon atoms, either two groups of R^2 may be bonded via an alkylene group of 2 to 8 carbon atoms, X is a halogen or hydrogen atom or a hydrocarbon moiety of 1 to 24 carbon atoms, and p and r are $2 \leq p \leq 4$, $0 \leq r \leq 2$, and $p + r = 4$, the modified organoaluminum resulting from reaction of an organoaluminum compound and water and having in the molecule one or more Al-O-Al bonds.

The invention further provides a process for producing polyolefins which comprises homopolymerizing an olefin or copolymerizing two or more olefins in the presence of a catalyst comprising a solid catalyst component and a modified organoaluminum compound, the solid catalyst component derived from mutual contact of (a) an inorganic porous oxide, (b) a compound of the formula $Al(OR^1)_nX_{3-n}$ where R^1 is a hydrocarbon group of 1 to 24 carbon atoms, X is a halogen atom, and n is $0 < n \leq 3$, and (c) a compound of the formula $R^2_pMX_r$, where M is a Group IVa metal, R^2 is a cyclopentadienyl, substituted cyclopentadienyl, indenyl or substituted indenyl group or an aralkyl group of 7 to 24 carbon atoms, either two groups of R^2 may be bonded via an alkylene group of 2 to 8 carbon atoms, X is a halogen or hydrogen atom or a hydrocarbon residue of 1 to 24 carbon atoms, and p and r are $2 \leq p \leq 4$, $0 \leq r \leq 2$ and $p + r = 4$, and (d) a magnesium halide, the modified organoaluminum compound resulting from reaction of an organoaluminum compound and water and having in the molecule one or more Al-O-Al bonds.

The catalyst according to the present invention is comprised of a solid catalyst component of a specified composition and a modified organoaluminum compound of a specified structure.

The solid catalyst component used herein may be derived by mutual contact of three members, i.e. (a) an inorganic porous oxide, (b) an $Al(OR^1)_nX_{3-n}$ compound and (c) an $R^2_pMX_r$ compound.

Compound (a) as a porous oxide has a surface area of 50 to 1,000 m²/g, preferably 100 to 500 m²/g, more

preferably 150 to 350 m²/g, and a pore volume of 0.5 to 3.0 cm³/g, preferably 1.0 to 2.5 cm³/g, more preferably 1.5 to 2.5 cm³/g. This compound may be chosen from silica, alumina, silica-alumina, titania, zirconia and tria either alone or in combination. Silica and alumina are particularly preferred. Any given oxide commercially obtained can be used as it is, or may be conveniently pretreated with heat in an inert gas or dried for example

from 150 to 800°C, preferably 200 to 600°C, and for 0.5 to 10 hours, preferably 2 to 5 hours.

Compound (b) is a compound of the formula $Al(OR^1)_nX_{3-n}$ where R^1 is a hydrocarbon group of a carbon number of 1 to 24, preferably 1 to 12, such as an alkyl, aryl or aralkyl group or the like, X is a halogen atom, and n is $0 < n \leq 3$. Specific examples of compound (b) include trimethoxyaluminum, dimethoxymonochloroaluminum, methoxydichloroaluminum, triethoxyaluminum, diethoxymonochloroaluminum, ethoxydichloroaluminum, triisopropoxyaluminum, diisopropoxymonochloroaluminum, isopropoxydichloroaluminum, tri-n-butoxyaluminum, di-n-butoxymonochloroaluminum, n-butoxydichloroaluminum, tri-sec-butoxyaluminum, di-sec-butoxymonochloroaluminum, sec-butoxydichloroaluminum, tri-pentoxymonochloroaluminum, dipentoxymonochloroaluminum, triphenoxyaluminum, diphenoxymonochloroaluminum, monophenoxymonochloroaluminum, ditolyloxyaluminum, ditolyloxymonochloroaluminum, tolyloxydichloroaluminum, tribenzyloxyaluminum and the like. Particularly preferred are triethoxyaluminum, triisopropoxyaluminum and tri-n-butoxyaluminum.

Compound (c) is such of the formula $R_p^2MX_r$, where M is a Group IVA transition metal, R^2 is a cyclopentadienyl, substituted cyclopentadienyl, indenyl or substituted indenyl group or an aralkyl group of a carbon number of 7 to 24, preferably 7 to 13, either two groups of R^2 may be bonded via an alkylene group of a carbon number of 2 to 8, preferably 2 to 4, X is a chlorine, bromine or fluorine atom, a hydrogen atom or a hydrocarbon moiety of a carbon number of 1 to 24, preferably 1 to 12, and p and r are $2 \leq p \leq 4$, $0 \leq r \leq 2$, and $p + r = 4$.

Suitable substituents for use in the substituted cyclopentadienyl and substituted indenyl groups of R^2 may be selected from an alkyl group of 1 to 6 carbon atoms, such as a methyl, ethyl or propyl group or the like, and a hydrogen atom. Aralkyl groups of R^2 include a benzyl, phenethyl, benzhydryl, trityl, phenethylbutyl and phenethylpropyl groups and the like. In the case where an alkylene group is present in compound (c), R^2 is either two of cyclopentadienyl, substituted cyclopentadienyl, indenyl and substituted indenyl groups. Hydrocarbon moieties as X include an alkyl group such as methyl, ethyl, propyl or the like, an aryl group such as phenyl, tolyl or the like, an aralkyl group such as benzyl, phenethyl, benzhydryl, trityl, phenylbutyl, phenylpropyl or the like, an ethoxy group, an propoxy group, a phenoxy group, an aryloxy group and the like. When r in the $R_p^2MX_r$ formula is equal to 2, X is the same or different.

Specific examples of compound (c) include

- bis(cyclopentadienyl)dichlorotitanium,
- bis(cyclopentadienyl)methylchlorotitanium,
- bis(cyclopentadienyl)dimethyltitanium,
- bis(cyclopentadienyl)ethoxychlorotitanium,
- bis(cyclopentadienyl)propoxychlorotitanium,
- bis(cyclopentadienyl)phenoxychlorotitanium,
- bis(cyclopentadienyl)propylchlorotitanium,
- bis(cyclopentadienyl)diphenyltitanium,
- bis(cyclopentadienyl)ditolyltitanium,
- bis(cyclopentadienyl)titaniumbenzyl,
- bis(cyclopentadienyl)titanium monochloromonohalide,
- bis(methylcyclopentadienyl)dimethyltitanium,
- tetracyclopentadienyltitanium,
- bis(indenyl)dichlorotitanium,
- bis(indenyl)dimethyltitanium,
- ethylene bis(indenyl)titanium dichloride,
- ethylene bis(tetrahydroindenyl)titanium dichloride,
- tetraneopentyltitanium, tetraneophyltitanium,
- tetrabenzyltitanium,
- bis(cyclopentadienyl)-dichlorozirconium,
- bis(cyclopentadienyl)methylchlorozirconium,
- bis(cyclopentadienyl)dimethylzirconium,
- bis(indenyl)dimethylzirconium,
- bis(indenyl)dichlorozirconium,
- ethylene bis(indenyl)dimethylzirconium,
- ethylene bis(indenyl)dichlorozirconium,

ethylene bis(tetrahydroindenyl)dichlorozirconium,
 bis(methylcyclopentadienyl)dimethylzirconium,
 bis(cyclopentadienyl)zirconium monochloromonohalide,
 bis(cyclopentadienyl)zirconiumbenzyl,
 5 tetracyclopentadienylzirconium, tetrabenzylzirconium,
 bis(cyclopentadienyl)ethoxychlorozirconium,
 bis(cyclopentadienyl)propoxychlorozirconium,
 bis(cyclopentadienyl)phenoxychlorozirconium,
 bis(cyclopentadienyl)propylchlorozirconium,
 10 bis(cyclopentadienyl)diphenylzirconium,
 bis(cyclopentadienyl)citrylzirconium,
 bis(cyclopentadienyl)monomethylmonohalide zirconium,
 bis(cyclopentadienyl)monoethylmonochloride zirconium,
 bis(cyclopentadienyl)monophenylmonochloride zirconium,
 15 tetraneopentylzirconium, tetraneophenylzirconium,
 bis(cyclopentadienyl)dimethylhafnium,
 bis(cyclopentadienyl)dichlorohafnium,
 bis(cyclopentadienyl)methylchlorohafnium,
 bis(cyclopentadienyl)ethylchlorohafnium,
 20 bis(cyclopentadienyl)propylchlorohafnium,
 bis(cyclopentadienyl)phenylchlorohafnium,
 bis(cyclopentadienyl)diphenylhafnium,
 bis(cyclopentadienyl)ditolylhafnium,
 bis(cyclopentadienyl)monochlorohalide hafnium,
 25 bis(cyclopentadienyl)monomethylhalide hafnium,
 bis(cyclopentadienyl)dibenzylhafnium,
 ethylene bis(indenyl)dichlorohafnium,
 ethylene bis(tetrahydroindenyl)dichlorohafnium, tetraneopentylhafnium, tetraneophylhafnium and the like.
 These compounds may be used singly or put together. By better choice taken among the listed compounds
 30 are bis(cyclopentadienyl)dichlorotitanium,
 bis(cyclorodienyl)dimethyltitanium,
 bis(cycloropentadienyl)dichlorohafnium,
 bis(cyclopentadienyl)dimethylhafnium,
 ethylene bis(indenyl)dichlorozirconium and ethylene bis(indenyl)dimethylzirconium.

35 The solid catalyst component contemplated under the invention are obtained by bringing compounds (a), (b) and (c) into contact with one another. Either one of the following sequences of contact is suitable for the formation of the catalyst component.

- (1) simultaneous contact of compounds (a), (b) and (c)
- (2) contact of compounds (a) and (b), followed by compound (c)
- 40 (3) contact of compounds (a) and (c), followed by compound (b)

The contact of compounds (a) to (c) may be effected, though not restricted, at from 0 to 200°C, preferably 50 to 100°C, and for 5 minutes to 30 hours, preferably 30 minutes to 10 hours, in the presence of an organic solvent typically chosen from inert hydrocarbons such as heptane, hexane, pentane, nonane, benzene, toluene and the like, alcohols, phenols, ethers, ketones, esters, amines, nitriles and halogen-containing compounds
 45 such as 1,2-dichloroethane, tetrachloroethane, ethylidene chloride, carbon tetrachloride, chloroform, chlorobenzene, dichlorobenzene and the like and polar solvents, either alone or in combination. After completion of the contact, the solvent may be removed as by evaporation.

More convenient is sequence (2) among the above sequences of contact. To conduct sequence (2), compounds (a) and (b) may be contacted by impregnating into compound (a) a solution of compound (b) previously
 50 dissolved in either one of the above listed solvents, or by dissolving both compounds together in the solvent. Contact conditions may be set at from 0 to 200°C, preferably 20 to 100°C, and for 5 minutes to 30 hours, preferably 30 minutes to 20 hours. The concentration of compound (b) ranges from 0.1 to 5 mol per liter of solvent, preferably 0.5 to 1.5 mol, and the amount of compound (b) is in the range 0.01 to 5 mmol per gram of compound (a), preferably 0.1 to 1.5 mmol. While in contacting compound (b) would presumably partially react with compound (a).
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Compound (a) in which compound (b) has been contained in a predetermined proportion may be suitably washed with a similar solvent and then brought into contact with compound (c). In such instance compound (a) may be previously dried or may be employed as prepared in dispersion form. Compound (a) thus treated

may be contacted with compound (c) with stirring in either one of the above listed solvents for example at from 20 to 200°C, preferably 50 to 100°C, and for 5 minutes to 30 hours, preferably 30 minutes to 10 hours, followed by removal of the solvent. The content of compound (c) in the resulting catalyst component is in the range of 0.1 to 10% by weight in terms of a transition metal, preferably 0.5 to 8.0% by weight.

Advantageously, by varying the content of compound (b) of the $\text{Al}(\text{OR}^1)_n\text{X}_{3-n}$ formula, polymers to be formed can be adjusted, at will, in their melting points which are associated with polymer processing.

The modified organoaluminum compound according to the invention results from reaction of an organoaluminum compound with water, and it has in the molecule an Al-O-Al bond within the number of 1 to 100, preferably 1 to 50. Reaction may be made usually in an inert hydrocarbon chosen from an aliphatic hydrocarbon such as pentane, hexane, heptane or the like, an alicyclic hydrocarbon such as cyclohexane or the like, or an aromatic hydrocarbon such as benzene, toluene, xylene or the like, among which aliphatic and aromatic hydrocarbons are particularly preferred.

Suitable organoaluminum compounds are those of the formula $\text{R}^3\text{AlX}_{3-n}$ where R^3 is a hydrocarbon group such as an aralkyl group of a carbon number of 1 to 18, preferably 1 to 12, or an alkenyl, aryl or aralkyl group, X is a halogen or hydrogen atom, and n is $1 \leq n \leq 3$. Trialkylaluminums are typical in which the alkyl group is a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, octyl, decyl or dodecyl group. Methyl among these groups is more suitable.

The molar ratio of water to organoaluminum compound may be in the range of 0.25:1 to 1.2:1, preferably 0.5:1 to 1:1. Reaction conditions may be at from -70 to +100°C, preferably -20 to +20°C, and for 5 to 48 hours, preferably 10 to 24 hours. Coreactive water may be one attached as the water of crystallization to copper sulfate hydrate, aluminum sulfate hydrate or the like.

A modified form of catalyst according to the invention is comprised of a solid catalyst component in which a magnesium halide is further incorporated as compound (d). Various other constituting compounds are as specified in connection with the first-mentioned form of catalyst.

Compound (d) is magnesium fluoride, magnesium chloride, magnesium bromide or magnesium iodide, each being substantially anhydrous, either alone or in combination. This compound may be treated with an electron donor such as an alcohol, ester, ketone, carboxylic acid, ether, amine, phosphine or the like.

To prepare the solid catalyst component for use in the modified catalyst, compound (a) to (d) are mutually contacted by the sequences of contact given below.

- (4) simultaneous contact of compounds (a), (b), (c) and (d)
- (5) contact of compound (a) with compound (d), (b) and (c) in the order mentioned
- (6) contact of compounds (a) and (b), followed by compounds (d) and (c)
- (7) contact of compounds (d) and (b), followed by compounds (a) and (c)
- (8) contact of compounds (b) and (c), followed by compounds (d) and (a)
- (9) contact of compounds (d), (b) and (c), followed by compound (a)

Sequence (7) is particularly preferred. Contacting may be done with stirring in an organic solvent at from 20 to 200°C, preferably 50 to 100°C, and for 5 minutes to 30 hours, preferably 30 minutes to 10 hours, after which the solvent is removed. The solvent may be suitably selected from those specified with regard to sequences (1) to (3). Alternatively, copulverization is feasible by ball milling, vibration milling, rod milling or impact milling with or without use of solvent and at from -20 to +200°C, preferably 50 to 100°C, and for 10 minutes to 50 hours, preferably 30 minutes to 30 hours.

Solvent contact is preferred to contact compounds (a) and (b), or compounds (b) and (c) in the presence of a solvent such as an inert hydrocarbon, halogen-containing compound or polar solvent as listed above. Copulverization contact is convenient in contacting compounds (d) and (b), or compounds (d), (b) and (c).

Compound (d) ranges in amount from 0.1 to 5 mmol per gram of compound (a), preferably 0.5 to 2 mmol, and compound (b) from 0.1 to 2 mmol per gram of compound (a), preferably 0.15 to 1.5 mmol. The content of compound (c) in the resultant catalyst component is between 0.5 and 10% by weight in terms of a transition metal, preferably between 0.1 and 8.0% by weight.

The process according to the invention is designed to homopolymerize or copolymerize olefins in the presence of the above specified catalyst. Into the reaction system a given solid catalyst component and a given modified organoaluminum compound may be put independently or as previously admixed. The catalyst component is used in an amount of 1 to 1,000,000, preferably 5 to 1,000, in an atomic ratio of transition metal to aluminum.

The process of the invention is applicable to all the olefins polymerizable with use of Ziegler type catalysts. It is suitable particularly for use in the homopolymerization of α -olefins of a carbon number of 2 to 12 such as ethylene, propylene, butene-1, hexene-1, 4-methylpentene-1 and the like and also in the copolymerization of ethylene with an α -olefins other than ethylene. α -Olefins as comonomers have a carbon number of 3 to 12,

preferably 3 to 6, and include propylene, butene-1, hexene-1, 4-methylpentene-1 and the like. Propylene-butene-1 and ethylene-two or more α -olefins are also copolymerizable.

To further improve the end polymer from the physical point of view, the olefin may be copolymerized with a diene compound such as butadiene, 1,4-hexadiene, ethylidene norbornene, dicyclopentadiene or the like.

The amount of the comonomer used is not specifically restricted but may be set usually at not more than 40% by mol, preferably less than 30% by mol, more preferably below 20% by mol.

The process of the invention is implemented by slurry, solution and gas phase polymerizations. Particularly preferred is gas phase polymerization usually conducted under oxygen-free, moisture-free conditions and with or without addition of an inert hydrocarbon. In the absence of the hydrocarbon, it is convenient to employ a gas phase method of a fluidized bed type in which reaction is made while polymers having been formed are maintained in a fluidized state, or a gas phase method of a stirring type. Continuous- or batch-type operation is possible. Reaction temperatures may be at from 20 to 200°C, preferably 50 to 100°C, reaction pressures at from atmospheric to 70 kg/cm²G, preferably atmospheric to 20 kg/cm²G, and reaction times at from 5 minutes to 10 hours, preferably 10 minutes to 5 hours.

The molecular weight of a homopolymer or copolymer to be formed may be adjusted by feeding a predetermined amount of hydrogen into the reaction system. Hydrogen feeding is more efficient than controlling the reaction temperatures and catalyst proportions.

According to the process of the invention, polymerization can be done with two or more stages of varied hydrogen concentrations, reaction temperatures and other parameters.

The invention will be further described by way of the following examples which should be regarded as illustrative but not as restrictive.

As shown in Tables 1 and 2, different catalysts were prepared and used to produce test ethylene- α -olefin copolymers. All the polymers were checked for a set of physical characteristics under the conditions given below and with the results listed in Tables 3 and 4 along with the respective catalytic activities in terms of gram polymer per gram transition metal.

Melt Index (MI)

ASTM D1238-57T was followed at two varied loads at 190°C, 2.16 kg (MI^{2.16}) and 10 kg (MI¹⁰).

Die Swell Ratio (DSR)

MI tester was used with the following equation.

$$R = \frac{A}{B}$$

R : die swell ratio

A : outside diameter of strand in MI measurement

B : inside diameter of orifice (2.1 mm)

Density (D)

Measurement was made by the ASTM D1505-68 procedure.

Melting Point (MP) by Differential Scanning Calorimetry (DSC)

On Seiko Electronics' DSC-20 tester a 5-mg portion of the test polymer was left at 180°C for 3 minutes, cooled at 0°C with a temperature drop of 10°C/min and allowed to stand at 0°C for 10 minutes, followed by heating with a temperature rise of 10°C/min.

Preparation of Methylalumoxane as Modified Organoaluminum Compound

In a 300-ml three-necked flask equipped with an electromagnetic stirrer were placed 13 g of copper sulfate, CuSO₄·5H₂O, and 50 ml of toluene. The mixture after being suspended was incorporated dropwise at 0°C and over 2 hours with 150 ml of a 1 mmol/ml trimethylaluminum solution. Reaction was effected at 25°C for 24 hours. Filtration of the reaction mixture and subsequent evaporation of excess toluene gave 4 g of the title compound in white crystalline form.

Preparation of Tetrabenzylzirconium as $R_p^2MX_r$ Compound

Into a 1-liter three-necked flask equipped with an electromagnetic stirrer were taken at 0°C and in a nitrogen atmosphere 500 ml of a diethyl ether solution in which 70 g of benzylmagnesium chloride was dissolved. 30 g of zirconium tetrachloride was thereafter added over 30 minutes at the same temperature and in the same atmosphere. The mixture was stirred for 2 hours while the temperature was being elevated to room temperature. After addition of 300 ml of decalin, stirring was continued at room temperature for one hour. Magnesium chloride having been formed was separated, and the resultant decalin solution was heated at 50°C to remove ether by nitrogen blowing. There was obtained 32 g of the title compound.

Preparation of Catalyst Component A

In a 300-ml three-necked flask equipped with an electromagnetic stirrer was placed 20 g of silica, SiO_2 , (Grade No. 952, Fuji-Davison Co.), the silica having been calcined at 460°C. A solution of triisopropoxyaluminum, $Al(OiPr)_3$, was added at room temperature, which solution was prepared by dissolving 2 g of $Al(OiPr)_3$ in 100 ml of n-hexane. The mixture was stirred in a nitrogen atmosphere and at 50°C for 2 hours, followed by separation of the supernatant, by washing with 100 ml of n-hexane and by drying through nitrogen blowing. The residue was incorporated with a solution of bis(cyclopentadienyl)dichlorotitanium, Cp_2TiCl_2 , in a nitrogen atmosphere and at room temperature, which solution was prepared by dissolving 1.2 g of Cp_2TiCl_2 in 70 ml of 1,2-dichloroethane. Subsequent stirring was done at room temperature for 2 hours after which the solvent was removed by nitrogen blowing at 50°C. The resultant catalyst component showed a titanium content of 1.03% by weight.

Preparation of Catalyst Component B

The procedure of catalyst component A was followed except that $Al(OiPr)_3$ was varied in amount from 2.0 g to 4.0 g. The resulting solid component was in a titanium content of 0.95% by weight.

Preparation of Catalyst Component C

The procedure of catalyst component A was followed except that 0.73 g of bis(cyclopentadienyl)dichlorozirconium, Cp_2ZrCl_2 , was used in place of Cp_2TiCl_2 and dissolved in 100 ml of toluene. The resulting solid component had a zirconium content of 0.99% by weight.

Preparation of Catalyst Component D

The procedure of catalyst component C was followed except for the use of $Cp_2Zr(CH_3)_2$ in an amount of 0.8 g. The resulting solid component had a zirconium content of 1.0% by weight.

Preparation of Catalyst Component E

The procedure of catalyst component A was followed except that 2.5 g of tri-sec-butoxyaluminum, $Al(Osec-Bu)_3$, was used in place of $Al(OiPr)_3$ and that the amount of Cp_2TiCl_2 was changed from 1.2 g to 2.6 g. The resulting solid component was 2.0% by weight in titanium content.

Preparation of Catalyst Component F

The procedure of catalyst component A was followed except that SiO_2 calcined at 600°C was used and that 1 g of bis(cyclopentadienyl)dimethyltitanium, Cp_2TiMe_2 , in 100 ml of toluene was substituted for Cp_2TiCl_2 . A solid component was obtained with a titanium content of 1.03 % by weight.

Preparation of Catalyst Component G

The procedure of catalyst component F was followed except that 0.65 g of bis(cyclopentadienyl)dimethylzirconium, Cp_2ZrMe_2 , was used in place of Cp_2TiMe_2 . There was provided a solid component of 1.0% by weight in zirconium content.

Preparation of Catalyst Component H

The procedure of catalyst component A was followed except for the use of 1.8 g of diisopropoxyaluminum chloride, $\text{Al}(\text{OiPr})_2\text{Cl}$, in place of $\text{Al}(\text{OiPr})_3$ with the result that a solid component was given with a titanium content of 1.05% by weight.

Preparation of Catalyst Component I

The procedure of catalyst component A was followed except that 1.2 g of tetrabenzylzirconium, $(\text{Bz})_4\text{Zr}$, was used in place of Cp_2TiCl_2 and dissolved in a mixture of 50 ml of toluene and 50 ml of decalin. There was obtained a solid component with a zirconium content of 0.98% by weight.

Preparation of Catalyst Component J

The procedure of catalyst component A was followed except for the use of 0.5 g of bis(dicyclopentadienyl)dichlorohafnium, Cp_2HfCl_2 . The resulting solid component was 0.99% by weight in hafnium content.

Preparation of Catalyst Component K

The procedure of catalyst component A was followed except for the use of 1.75 g of bis(indenyl)dichlorotitanium, $(\text{Ind})_2\text{TiCl}_2$, so that a solid component was obtained with a titanium content of 1% by weight.

Preparation of Catalyst Component L

In a 400-ml stainless steel pot, provided therein with 25 stainless steel balls of 1/2 inch in diameter, were placed 10 g of $\text{Al}(\text{OiPr})_3$ and 0.55 g of Cp_2TiCl_2 . Ball milling was effected in a nitrogen atmosphere and at room temperature for 16 hours, thereby giving a solid component of 1.0% by weight in titanium content.

Preparation of Catalyst Component M

In a 300-ml three-necked flask equipped with an electromagnetic stirrer was placed 20 g of Grade No. 952 SiO_2 calcined at 460°C . 1.1 g of Cp_2TiCl_2 in 70 ml of 1,2-dichloroethane was thereafter added in a nitrogen atmosphere and at room temperature. Stirring was done at room temperature for 2 hours, followed by removal of the solvent by nitrogen blowing at 50°C . The resulting solid component had a titanium content of 1.0% by weight.

Catalyst components A to K were inventive and catalyst components L and M comparative.

Inventive Example 1

In a 3-liter stainless steel autoclave which had been replaced with nitrogen were 20 g of polyethylene pellet seed, 100 mg of catalyst component A and 3.9 ml of methylalumoxane, MAO, in a 2.7 mmol/ml solution. The mixture was stirred at 60°C , followed by charge of a combined gas of ethylene and butene-1 at 9 kg/cm²G. The mol ratio of butene-1 to ethylene was 0.25. Polymerization was conducted for 2 hours with continuous feeding of the gas in a mol ratio of butene-1 to ethylene of 0.05 and at a total pressure of 9 kg/cm²G. After completion of the reaction, the system was purged of excess gas and then cooled to remove the seed, thereby providing 43 g of a white polymer.

Inventive Examples 2 to 11

The method of Inventive Example 1 was followed except for the use of catalyst components B to K, respectively.

Comparative Example 1

The method of Inventive Example 1 was followed except that 10 mg of Cp_2TiCl_2 was used in place of catalyst component A with MAO varied in amount from 3.9 ml to 7.4 ml.

Comparative Examples 2 and 3

The method of Inventive Example 1 was followed except for the use of catalyst components L and M, respectively.

Comparative Example 4

The method of Comparative Example 1 was followed except that the amount of MAO was varied at 6.3 ml.

Preparation of Catalyst Component AA(1) Copulverization of MgCl_2 with $\text{Al}(\text{OC}_2\text{H}_5)_3$

Into a 400-ml stainless steel pot in which were contained 25 stainless steel balls of 1/2 inch in diameter were taken 10 g of magnesium chloride anhydride, MgCl_2 , and 3.83 g of triethoxyaluminum, $\text{Al}(\text{OC}_2\text{H}_5)_3$. Ball milling was effected in a nitrogen atmosphere and at room temperature for 16 hours, followed by dissolution of 2.63 g of the resulting copulverizate in 80 ml of anhydrous tetrahydrofuran.

(2) Deposition on SiO_2

In a 300-ml three-necked flask equipped with an electromagnetic stirrer were placed in a nitrogen atmosphere and at room temperature 10 g of Grade No. 952 SiO_2 calcined at 460°C and 80 ml of the tetrahydrofuran solution prepared above. After being stirred at room temperature for 2 hours, the mixture was reacted with refluxing for 3 hours. On separation of the supernatant the solvent was removed by nitrogen blowing. To the residue was added in a nitrogen atmosphere and at room temperature 0.7 g of Cp_2TiCl_2 dissolved in 70 ml of 1,2-dichloroethane. Stirring was continued at room temperature for 2 hours after which the solvent was nitrogen-blown at 50°C . The resulting solid component had titanium contained in an amount of 1.02% by weight.

Preparation of Catalyst Component BB(1) Copulverization of MgCl_2 with $\text{Al}(\text{OC}_2\text{H}_5)_3$

The procedure of catalyst component AA was followed except that $\text{Al}(\text{OC}_2\text{H}_5)_3$ was varied in amount from 3.83 g to 8.5 g. 5.3 g of the resultant copulverizate was dissolved in 160 ml of anhydrous tetrahydrofuran.

(2) Deposition on SiO_2

The procedure of catalyst component AA was followed except for the use of 160 ml of tetrahydrofuran and of 0.83 g of Cp_2TiCl_2 . A solid component was obtained with a titanium content of 0.98% by weight.

Preparation of Catalyst Component CC(1) Copulverization of MgCl_2 with $\text{Al}(\text{OC}_2\text{H}_5)_3$

The procedure of catalyst component AA was followed except that the amount of $\text{Al}(\text{OC}_2\text{H}_5)_3$ was changed to 4.9 g. 1.42 g of the copulverizate thus formed was dissolved in 50 ml of anhydrous tetrahydrofuran.

(2) Deposition on SiO_2

The procedure of catalyst component AA was followed except that tetrahydrofuran and Cp_2TiCl_2 were varied in amount at 50 ml and at 0.62 g, respectively. The resulting solid catalyst was 1.03% by weight in titanium content.

Preparation of Catalyst Component DD

The procedure of catalyst component AA was followed except for the use of 0.42 g of Cp_2ZrCl_2 in place of Cp_2TiCl_2 whereby a solid component was prepared with a zirconium content of 1.0% by weight.

Preparation of Catalyst Component EE(1) Copulverization of MgCl_2 with $\text{Al}(\text{OiC}_3\text{H}_7)_3$

The procedure of catalyst component AA was followed except that 4.8 g of $\text{Al}(\text{OiC}_3\text{H}_7)_3$ was substituted for $\text{Al}(\text{OC}_2\text{H}_5)_3$. 2.8 g of the resulting copulverizate was dissolved in 80 ml of anhydrous tetrahydrofuran.

(2) Deposition on SiO_2

The procedure of catalyst component AA was followed except that tetrahydrofuran was used in an amount of 80 ml. A solid component was provided with a titanium content of 0.99% by weight.

Preparation of Catalyst Component FF

In a 300-ml three-necked flask equipped with an electromagnetic stirrer were placed at room temperature 10 g of Grade No. 925 SiO_2 calcined at 460°C and 0.6 g of $\text{Al}(\text{OiC}_3\text{H}_7)_3$ dissolved in 100 ml of n-hexane. The mixture was stirred in a nitrogen atmosphere and at 50°C for 2 hours, followed by separation of the supernatant, by washing with 100 ml of n-hexane and by nitrogen blowing. The dry residue was incorporated with 0.95 g of MgCl_2 dissolved in 80 ml of anhydrous ethanol and thereafter stirred at room temperature for 2 hours. Nitrogen blowing was done at 50°C and in vacuo drying at 100°C for 2 hours. 0.63 g of Cp_2TiCl_2 dissolved in 70 ml of 1,2-dichloroethane was added in a nitrogen atmosphere and at room temperature. After stirring at room temperature, the solvent was nitrogen-blown at 50°C . The resulting solid component had a titanium content of 1.0% by weight.

Preparation of Catalyst Component GG(1) Reaction of $\text{Al}(\text{OiC}_3\text{H}_7)_3$ with Cp_2TiCl_2

Into a 300-ml three-necked flask equipped with an electromagnetic stirrer were put 0.46 g of $\text{Al}(\text{OiC}_3\text{H}_7)_3$ and 0.62 g of Cp_2TiCl_2 and then 100 ml of 1,2-dichloroethane. Reaction was made with refluxing for 2 hours.

(2) Deposition on SiO_2

In a similar flask were placed 10 g of Grade No. 952 SiO_2 calcined at 460°C and 0.95 g of MgCl_2 dissolved in 150 ml of ethanol. After 2-hour stirring at room temperature for 2 hours the mixture was nitrogen-blown at 50°C and then vacuum-dried. To the residue was added in a nitrogen atmosphere and at room temperature 100 ml of the reaction solution prepared above. Stirring was continued at room temperature for 2 hours, followed by nitrogen blowing at 50°C , so that a solid component was provided with a titanium content of 0.98% by weight.

Preparation of Catalyst Component HH(1) Copulverization of MgCl_2 with $\text{Al}(\text{OiC}_3\text{H}_7)_3$ and Cp_2TiCl_2

The procedure of catalyst component AA was followed except that MgCl_2 was varied in amount from 3.83 g to 4.75 g and that 3 g of $\text{Al}(\text{OiPr})_3$ was substituted for $\text{Al}(\text{OC}_2\text{H}_5)_3$ with 3.15 g of Cp_2TiCl_2 further added. 2.18 g of the resultant copulverizate was suspended in 150 ml of anhydrous ethanol.

(2) Deposition on SiO_2

The procedure of catalyst component AA was followed except that tetrahydrofuran was replaced by ethanol, whereby a solid component was prepared with a titanium content of 1.0% by weight.

Preparation of Catalyst Components II, JJ, KK, LL and MM

The procedure of catalyst component AA was followed except that the compounds shown in Table 2 were used in place of Cp_2TiCl_2 .

Preparation of Catalyst Components NN, OO and PP

The procedure of catalyst component AA was followed except the use of the compounds of Table 2 in place of SiO_2 .

Preparation of Catalyst Component QQ

The procedure of catalyst component AA was followed except that $\text{Al}(\text{OC}_2\text{H}_5)_3$ was replaced by $\text{Al}(\text{OiC}_3\text{H}_7)_2\text{Cl}$.

Preparation of Catalyst Component RR

Into a 300-ml three-necked flask equipped with an electromagnetic stirrer were taken in a nitrogen atmosphere and at room temperature 20 g of Grade No. 952 SiO_2 calcined at 460°C and 1.1 g of Cp_2TiCl_2 dissolved in 70 ml of 1,2-dichloroethane. After 2-hour stirring at room temperature the mixture was nitrogen-blown at 50°C to remove the solvent. A solid component was prepared with a titanium content of 1.0% by weight.

Preparation of Catalyst Component SS

In a similar flask were placed at room temperature 20 g of Grade No. 952 SiO_2 calcined at 460°C and 2.0 g of $\text{Al}(\text{OiP}_2)_3$ dissolved in 100 ml of n-hexane. Stirring was continued in a nitrogen atmosphere and at 50°C for 2 hours. On separation of the supernatant the reaction mixture was nitrogen-blown. To the dry residue was added in a nitrogen atmosphere and at room temperature 1.2 g of $(\text{Ind})_2\text{TiCl}_2$ dissolved in 70 ml of 1,2-dichloroethane, followed by stirring at room temperature and by nitrogen blowing at 50°C to thereby remove the solvent. The resulting solid component had a titanium content of 1.0% by weight.

Catalyst components AA to QQ were inventive and catalyst components RR and SS comparative. These inventive components were of a four-member composition in the solid catalyst component.

Inventive Example 12

The method of Inventive Example 1 was followed except that catalyst component AA was used in place of catalyst component A of a three-membered solid component. A white polymer was produced in an amount of 87 g.

Inventive Examples 13 to 18

The method of Inventive Example 12 was followed except for the use of catalyst components BB to QQ, respectively.

Comparative Examples 5 and 6

The method of Inventive Example 12 was followed except for the use of catalyst components RR and SS, respectively.

Table 1

run	solid catalyst component					org Al compd	Al/M (mol ratio)
	type	(a)	(b)	Al/(c) (mmol/g)	(c) (wt%)		
IE 1	A	SiO ₂	Al(OiPr) ₃	0.5	Cp ₂ TiCl ₂	MAO	500
2	B	"	"	1	"	"	"
3	C	"	"	0.5	Cp ₂ ZrCl ₂	"	"
4	D	"	"	1	"	"	"
5	E	"	Al(OsecBu) ₃	0.5	Cp ₂ TiCl ₂	"	"
6	F	"	Al(OiPr) ₃	"	Cp ₂ TiMe ₂	"	"
7	G	"	"	"	Cp ₂ ZrMe ₂	"	"
8	H	"	Al(OiPr) ₂ Cl	"	Cp ₂ TiCl ₂	"	"
9	I	"	Al(OiPr) ₃	"	(Bz) ₄ Zr	"	"
10	J	"	"	"	Cp ₂ HfCl ₂	"	"
11	K	"	"	"	(Ind) ₂ TiCl ₂	"	"
CE 1	-	-	-	-	Cp ₂ TiCl ₂	MAO	500
2	L	-	Al(OiPr) ₃	-	"	"	"
3	M	SiO ₂	-	-	"	"	"
4	-	-	-	-	Cp ₂ ZrCl ₂	"	"

IE: inventive example CE: comparative example

Table 2

run	type	solid catalyst component				(d)/(a) (mmol/g)	(b)/(a) (mmol/g)	(3M wt%)	org Al compd	Al/M (mol ratio)
		(a)	(b)	(c)	(d)					
IE 12	AA	SiO ₂	Al(OEt) ₃	Cp ₂ TiCl ₂	MgCl ₂	2	0.45	1.02	MAO	500
13	BB	"	"	"	"	3	1.5	0.98	"	"
14	CC	"	"	"	"	1	0.29	1.03	"	"
15	DD	"	"	Cp ₂ ZrCl ₂	"	2	0.45	1.0	"	"
16	EE	"	Al(OiPr) ₃	Cp ₂ TiCl ₂	"	2	0.45	0.99	"	"
17	FF	"	"	"	"	1	0.29	1.0	"	"
18	GG	"	"	"	"	"	"	0.98	"	"
19	HH	"	"	"	"	"	"	1.0	"	"
20	II	"	Al(OEt) ₃	Cp ₂ TiMe ₂	"	2	0.45	0.98	"	"
21	JJ	"	"	Cp ₂ ZrMe ₂	"	"	"	0.99	"	"
22	KK	"	"	(Bz) ₄ Zr	"	"	"	0.99	"	"
23	LL	"	"	Cp ₂ HfCl ₂	"	"	"	1.0	"	"
24	MM	"	"	(Ind) ₂ TiCl ₂	"	"	"	1.01	"	"
25	NN	Al ₂ O ₃	"	Cp ₂ TiCl ₂	"	"	"	1.05	"	"
26	OO	SiO ₂ -Al ₂ O ₃	"	"	"	"	"	0.97	"	"
27	PP	SiO ₂ -TiO ₂	"	"	"	"	"	0.98	"	"
28	QQ	SiO ₂	Al(OiPr) ₂ Cl	"	"	"	"	0.99	"	"
CE 5	RR	SiO ₂	-	Cp ₂ TiCl ₂	-	-	-	1.0	MAO	500
6	SS	"	Al(OiPr) ₃	"	-	-	0.5	1.0	"	"

Table 3

run	yield (g)	catalytic activity (g/gm)	MI2.16 (g/10 min)	DSR	bulk density (g/cc)	D (g/cm ²)	MP (°C, peak)
IE 1	43	43,000	1.9	1.93	0.42	0.915	93.9
2	39	39,000	1.4	1.92	0.43	0.919	94.1
3	48	48,000	9.4	1.78	0.41	0.911	98.0
4	44	44,000	9.0	1.76	0.41	0.914	98.3
5	79	40,000	2.0	1.82	0.42	0.921	95.1
6	34	34,000	1.3	1.89	0.41	0.923	95.4
7	50	50,000	8.8	1.71	0.43	0.919	110.2
8	36	36,000	8.7	1.87	0.41	0.924	95.5
9	20	20,000	1.3	1.69	0.38	0.928	111.6
10	21	21,000	0.45	1.81	0.39	0.916	94.0
11	41	41,000	1.8	1.83	0.40	0.918	94.0
CE 1	27	14,000	3.5	1.54	0.23	0.922	88.6
2	10	10,000	1.9	1.73	0.28	0.921	89.0, 124.3
3	19	19,000	2.2	1.55	0.36	0.924	89.0
4	75	24,000	37	1.58	0.21	0.911	97.9

Table 4

run	yield (g)	catalytic activity (g/gM)	MI2.16 (g/10 min)	DSR	bulk density (g/cc)	D (g/cm ²)	MP (°C, peak)
IE 12	87	85,000	1.8	1.87	0.42	0.925	83.1, 121.2
13	75	76,500	0.6	1.68	0.39	0.926	89.4, 121.6
14	96	93,000	3.1	1.78	0.44	0.928	92.0, 122.7
15	88	88,000	1.1	1.88	0.40	0.9222	110.2
16	80	81,000	2.0	1.86	0.41	0.920	90.1, 121.0
17	91	91,000	2.9	1.89	0.42	0.919	89.7, 121.0
18	65	66,000	0.8	1.67	0.40	0.920	89.5, 120.8
19	53	53,000	1.1	1.83	0.38	0.918	89.4, 120.6
20	73	74,500	3.4	1.92	0.39	0.923	91.2
21	81	82,000	1.6	1.74	0.42	0.919	107.1
22	29	29,000	2.3	1.79	0.38	0.929	118
23	39	39,000	0.35	1.60	0.41	0.926	110.3
24	68	67,000	1.4	1.83	0.41	0.919	92.0, 120.6
25	46	44,000	1.1	1.74	0.43	0.918	85.1, 120.4
26	34	35,000	0.8	1.63	0.40	0.920	86.2, 120.9
27	59	60,000	1.7	1.71	0.38	0.919	89.7, 121.0
28	81	82,000	1.5	1.76	0.38	0.920	89.4, 121.0
CE 5	16	16,000	2.2	1.55	0.36	0.924	89.0
6	43	43,000	1.9	1.93	0.42	0.915	93.9

Claims

1. A process for producing polyolefins which comprises homopolymerizing an olefin or copolymerizing two or more olefins in the presence of a catalyst comprising a solid catalyst component and a modified organoaluminum compound, the solid catalyst component derived from mutual contact of (a) an inorganic porous oxide, (b) a compound of the formula $\text{Al}(\text{OR}^1)_n\text{X}_{3-n}$ where R^1 is a hydrocarbon group of 1 to 24 carbon atoms, X is a halogen atom, and n is $0 < n \leq 3$, and (c) a compound of the formula R^2MX_r where M is a Group IVa metal, R^2 is a cyclopentadienyl, substituted cyclopentadienyl, indenyl or substituted indenyl group or an aralkyl group of 7 to 24 carbon atoms, either two groups of R^2 may be bonded via an alkylene group of 2 to 8 carbon atoms, X is a halogen or hydrogen atom or a hydrocarbon residue of 1 to 24 carbon atoms, and p and r are $2 \leq p \leq 4$, $0 \leq r \leq 2$ and $p + r = 4$, the modified organoaluminum compound resulting from reaction of an organoaluminum compound and water and having in the molecule one or more Al-O-Al bonds.
2. The process of claim 1 wherein compound (a) is silica, alumina, silica-alumina, titania, zirconia or tria or a combination thereof.
3. The process of claim 1 wherein compound (b) is trimethoxyaluminum, dimethoxymonochloroaluminum, methoxydichloroaluminum, triethoxyaluminum, diethoxymonochloroaluminum, ethoxydichloroaluminum, triisopropoxyaluminum, diisopropoxymonochloroaluminum, isopropoxydichloroaluminum, tri-n-butoxyaluminum, di-n-butoxymonochloroaluminum, n-butoxydichloroaluminum, tri-sec-butoxyaluminum, di-sec-butoxymonochloroaluminum, sec-butoxydichloroaluminum, tripentoxyaluminum, dipentoxymonochloroaluminum, pentoxydichloroaluminum, triphenoxyaluminum, diphenoxymonochloroaluminum, monophenoxydichloroaluminum, tritolyloxyaluminum, ditolyloxymonochloroaluminum, tolyloxydichloroaluminum or tribenzyloxyaluminum.
4. The process of claim 1 wherein compound (c) is bis(cyclopentadienyl)dichlorotitanium, bis(cyclopentadienyl)methylchlorotitanium, bis(cyclopentadienyl)dimethyltitanium, bis(cyclopentadienyl)ethoxychlorotitanium, bis(cyclopentadienyl)propoxychlorotitanium, bis(cyclopentadienyl)phenoxychlorotitanium, bis(cyclopentadienyl)propylchlorotitanium, bis(cyclopentadienyl)diphenyltitanium, bis(cyclopentadienyl)ditolytitanium, bis(cyclopentadienyl)titaniumbenzyl, bis(cyclopentadienyl)titanium monochloromonohalide, bis(methylcyclopentadienyl)dimethyltitanium, tetracyclopentadienyltitanium, bis(indenyl)dichlorotitanium, bis(indenyl)dimethyltitanium, ethylene bis(indenyl)titanium dichloride, ethylene bis(tetrahydroindenyl)titanium dichloride, tetraneopentyltitanium, tetraneophyltitanium, tetrabenzyltitanium, bis(cyclopentadienyl)dichlorozirconium, bis(cyclopentadienyl)methylchlorozirconium, bis(cyclopentadienyl)dimethylzirconium, bis(indenyl)dimethylzirconium, bis(indenyl)dichlorozirconium, ethylene bis(indenyl)dichlorozirconium,

ethylene bis(tetrahydroindenyl)dichlorozirconium,
 ethylene bis(indenyl)dimethylzirconium,
 bis(methylcyclopentadienyl)dimethylzirconium,
 bis(cyclopentadienyl)zirconium monochloromonohalide,
 5 bis(cyclopentadienyl)zirconiumbenzyl,
 tetracyclopentadienylzirconium, tetrabenzylzirconium,
 bis(cyclopentadienyl)ethoxychlorozirconium,
 bis(cyclopentadienyl)propoxychlorozirconium,
 bis(cyclopentadienyl)phenoxychlorozirconium,
 10 bis(cyclopentadienyl)propylchlorozirconium,
 bis(cyclopentadienyl)diphenylzirconium,
 bis(cyclopentadienyl)citrylzirconium,
 bis(cyclopentadienyl)monomethylmonohalide zirconium,
 bis(cyclopentadienyl)monoethylmonochloride zirconium,
 15 bis(cyclopentadienyl)monoqhenylmonochloride zirconium,
 tetraneopentylzirconium, tetraneophenylzirconium,
 bis(cyclopentadienyl)dimethylhafnium,
 bis(cyclopentadienyl)dichlorohafnium,
 bis(cyclopentadienyl)methylchlorohafnium,
 20 bis(cyclopentadienyl)ethylchlorohafnium,
 bis(cyclopentadienyl)propylchlorohafnium,
 bis(cyclopentadienyl)phenylchlorohafnium,
 bis(cyclopentadienyl)diphenylhafnium,
 bis(cyclopentadienyl)ditolylhafnium,
 25 bis(cyclopentadienyl)monochlorohalide hafnium,
 bis(cyclopentadienyl)monomethylhalide hafnium,
 bis(cyclopentadienyl)dibenzylhafnium,
 ethylene bis(indenyl)dichlorohafnium,
 ethylene bis(tetrahydroindenyl)dichlorohafnium,
 30 tetraneopentylhafnium or tetraneophylhafnium.

5. The process of claim 1 wherein the olefin is ethylene, propylene, butene-1, hexene-1 or 4-methylpentene-1 or a combination thereof.

35 6. A polyolefin produced by the process of claim 1.

7. A process for producing polyolefins which comprises homopolymerizing an olefin or copolymerizing two or more olefins in the presence of a catalyst comprising a solid catalyst component and a modified organoaluminum compound, the solid catalyst component derived from mutual contact of (a) an inorganic porous oxide, (b) a compound of the formula $\text{Al}(\text{OR}^1)_n\text{X}_{3-n}$ where R^1 is a hydrocarbon group of 1 to 24 carbon atoms, X is a halogen atom, and n is $0 < n \leq 3$, and (c) a compound the formula R^2_pMX_r , where M is a Group VIa metal, R^2 is a cyclopentadienyl, substituted cyclopentadienyl, indenyl or substituted indenyl group or an aralkyl group of 7 to 24 carbon atoms, either two groups of R^2 may be bonded via an alkylene group of 2 to 8 carbon atoms, X is a halogen or hydrogen atom or a hydrocarbon residue of 1 to 24 carbon atoms, and p and r are $2 \leq p \leq 4$, $0 \leq r \leq 2$ and $p + r = 4$, and (d) a magnesium halide, the modified organoaluminum compound resulting from reaction of an organoaluminum compound and water and having in the molecule one or more Al-O-Al bonds.

8. The process of claim 8 wherein compound (d) is magnesium fluoride, magnesium chloride, magnesium bromide or magnesium iodide or a combination thereof.

9. The process of claim 8 wherein compound (a) is silica, alumina, silica-alumina, titania, zirconia or tria or a combination thereof.

55 10. The process of claim 8 wherein compound (b) is trimethoxyaluminum, dimethoxymonochloroaluminum, methoxydichloroaluminum, triethoxyaluminum, diethoxymonochloroaluminum, ethoxydichloroaluminum, triisopropoxyaluminum, diisoproxyoxymonochloroaluminum, isoproxydichloroaluminum, tri-n-butoxyalumi-

num, di-n-butoxymonochloroaluminum, n-butoxydichloroaluminum, tri-sec-butoxyaluminum, di-sec-butoxymonochloroaluminum, sec-butoxydichloroaluminum, tripentoxylaluminum, dipentoxymonochloroaluminum, pentoxydichloroaluminum, triphenoxyaluminum, diphenoxymonochloroaluminum, monophenoxydichloroaluminum, tritolyloxylaluminum, ditolyloxymonochloroaluminum, tolyloxydichloroaluminum or tribenzylloxylaluminum.

11. The process of claim 8 wherein compound (c) is bis(cyclopentadienyl)dichlorotitanium,

bis(cyclopentadienyl)methylchlorotitanium,
 bis(cyclopentadienyl)dimethyltitanium,
 bis(cyclopentadienyl)ethoxychlorotitanium,
 bis(cyclopentadienyl)propoxychlorotitanium,
 bis(cyclopentadienyl)phenoxychlorotitanium,
 bis(cyclopentadienyl)propylchlorotitanium,
 bis(cyclopentadienyl)diphenyltitanium,
 bis(cyclopentadienyl)ditolyltitanium,
 bis(cyclopentadienyl)titaniumbenzyl,
 bis(cyclopentadienyl)titanium monochloromonohalide,
 bis(methylcyclopentadienyl)dimethyltitanium,
 tetracyclopentadienyltitanium,
 bis(indenyl)dichlorotitanium,
 bis(indenyl)dimethyltitanium,
 ethylene bis(indenyl)titanium dichloride,
 ethylene bis(tetrahydroindenyl)titanium dichloride,
 tetraneopentyltitanium, tetraneophyltitanium,
 tetrabenzyltitanium,
 bis(cyclopentadienyl)dichlorozirconium,
 bis(cyclopentadienyl)methylchlorozirconium,
 bis(cyclopentadienyl)dimethylzirconium,
 bis(indenyl)dimethylzirconium,
 bis(indenyl)dichlorozirconium,
 ethylene bis(indenyl)dichlorozirconium,
 ethylene bis(tetrahydroindenyl)dichlorozirconium,
 ethylene bis(indenyl)dimethylzirconium,
 bis(methylcyclopentadienyl)dimethylzirconium,
 bis(cyclopentadienyl)zirconium monochloromonohalide,
 bis(cyclopentadienyl)zirconiumbenzyl,
 tetracyclopentadienylzirconium, tetrabenzylzirconium,
 bis(cyclopentadienyl)ethoxychlorozirconium,
 bis(cyclopentadienyl)propoxychlorozirconium,
 bis(cyclopentadienyl)phenoxychlorozirconium,
 bis(cyclopentadienyl)propylchlorozirconium,
 bis(cyclopentadienyl)diphenylzirconium,
 bis(cyclopentadienyl)ditrylzirconium,
 bis(cyclopentadienyl)monomethylmonohalide zirconium,
 bis(cyclopentadienyl)monoethylmonochloride zirconium,
 bis(cyclopentadienyl)monophenylmonochloride zirconium,
 tetraneopentylzirconium, tetraneophenylzirconium,
 bis(cyclopentadienyl)dimethylhafnium,
 bis(cyclopentadienyl)dichlorohafnium,
 bis(cyclopentadienyl)methylchlorohafnium,
 bis(cyclopentadienyl)ethylchlorohafnium,
 bis(cyclopentadienyl)propylchlorohafnium,
 bis(cyclopentadienyl)phenylchlorohafnium,
 bis(cyclopentadienyl)diphenylhafnium,
 bis(cyclopentadienyl)ditolylhafnium,
 bis(cyclopentadienyl)monochlorohalide hafnium,
 bis(cyclopentadienyl)monomethylhalide hafnium,
 bis(cyclopentadienyl)dibenzylhafnium,

ethylene bis(indenyl)dichlorohalfnium,
ethylene bis(tetrahydroindenyl)dichlorohalfnium,
tetraneopentylhalfnium or tetraneophylhalfnium.

- 5 12. The process of claim 8 wherein the olefin is ethylene, propylene, butene-1, hexene-1 or 4-methylpentene-1
or a combination thereof.
13. A polyolefin produced by the process of claim 8.

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